BIODIESEL PRODUCTION VIA HOMOGENEOUS LEWIS ACID CATALYZED TRANSESTERIFICATION

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ABSTRACT

The transesterification of triglyceride mostly found in vegetable oils with methanol using homogeneous lewis acid is one of promising method to convert triglyceride into fatty acid methyl ester which is an alternative to replace fossil fuel as energy source mostly in transportation industry. The present study investigated the use of Tin (II) Chloride, $SnCl_2$ (Lewis acid catalyst) to catalyze the transesterification reaction of palm oil with methanol to fatty acid methyl ester (biodiesel) and the optimum conditions for biodiesel production. The conversion of palm oil to fatty acid methyl ester was analyzed by Gas Chromatography (GC). The analysis from Gas Chromatography showed that the conversion of triglycerides into fatty acid methyl esters using $SnCl_2$ as catalyst was affected by catalyst concentration, methanol to oil molar ratio and temperature. The optimum conditions to afford 92.67 % conversion of palm oil to fatty acid methyl ester (biodiesel) is with the use of 18 to 1 methanol to oil molar ratio and reaction time of 240 minutes at 85 ºC in the presence of 7wt % Tin (II) Chloride as catalyst.

ABSTRAK

Pengtransesteran trigliserida banyak ditemui di minyak sayuran dengan metanol menggunakan asid homogen Lewis yang merupakan salah satu cara untuk menukar trigliserida menjadi metil ester asid lemak yang merupakan alternatif untuk menggantikan bahan bakar fosil sebagai sumber tenaga terutama dalam industri pengangkutan. Penelitian ini bertujuan untuk menghasilkan metil ester asid lemak dengan menggunakan Tin (II) Chloride, $SnCl_2$ sebagai mangkin dan juga untuk menentukan keadaan optimum untuk pengeluaran metil ester melalui proses pengtransesteran. Data eksperimen menunjukkan hasil metil ester asid lemak dipengaruhi oleh pengaruh nisbah molar metanol minyak, pengaruh suhu dan pengaruh reaksi konsentrasi mangkin. Setelah percubaan telah dilakukan, keadaan yang paling optimum untuk pengtransesteran minyak bunga matahari dapat dicapai pada suhu reaksi 85 °C, nisbah molar metanol 18:1 untuk minyak dan 7wt % mangkin. Penukaran tertinggi dari keadaan ini adalah penukaran 92.67% metil ester asid lemak.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	ACKNOWLEDMENTS	**i**
	ABSTRACT	**ii**
	ABSTRAK	**iii**
	TABLE OF CONTENT	**iv-vi**
	LIST OF TABLE	**vii**
	LIST OF FIGURE	**viii**
	LIST OF SYMBOL	**ix**
	LIST OF APPENDICS	**x**
1	**INTRODUCTION**	**1**
	1.1 Background of Study	1-2
	1.2 Problem Statement	3
	1.3 Research Objectives	4

	1.4	Scope of Research	4
	1.5	Rationale & Significance of Study	4
2	**LITERATURE REVIEW**		**5**
	2.1	Biodiesel	5-7
	2.2	Method of Producing Biodiesel	7-8
		2.2.1 Direct Use and Blending	7-8
		2.2.2 Micro-emulsion	8
		2.2.3 Pyrolysis (Thermal Cracking)	8-9
		2.2.4 Esterification	9-10
		2.2.5 Transesterification	10-12
	2.3	Catalyst	12
		2.3.1 Homogeneous Catalyst	12-13
		2.3.1.1 Base-catalyzed Transesterification	13
		2.3.1.2 Acid-catalyzed Transesterification	14-15
		2.3.2 Heterogeneous Catalyst	15-16
		2.3.3 Enzyme Catalyst	16
	2.4	Solvent	17
3	**METHODOLOGY**		**18**
	3.1	Introduction	18
	3.2	Materials and Equipments	18
	3.3	Experimental Procedure	19
		3.3.1 Transesterification Reaction	19-20
		3.3.1.1 Effect of Temperature	20
		3.3.1.2 Effect of Catalyst Concentration	21

		3.3.1.3 Effect of Methanol to Oil Molar Ratio	21-22
		3.3.2 Settling	22
		3.3.3 Filtering	22
	3.4	Gas Chromatography Analysis	23
		3.4.1 Stock Standards	23-24
		3.4.2 Working Standards	24
		3.4.3 Procedure for Samples	24
4	**RESULTS AND DISCUSSIONS**		25
	4.1	The Effect of Temperature on the Conversion of Palm Oil to Methyl Ester.	25-28
	4.2	The Effect of Methanol to Oil Molar Ratio to the Conversion of Palm Oil to Methyl Ester.	29-31
	4.3	The Effect of Methanol to Oil Molar Ratio to the Conversion of Palm Oil to Methyl Ester.	31-34
5	**CONCLUSION AND RECOMMENDATIONS**		**35**
	5.1	Conclusion	35
	5.2	Recommendations	36-37
REFERENCES			**38-41**
APPENDICES			**42-48**

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Specification of diesel and biodiesel fuel	6
3.1	List of operating conditions for the study of the effect of temperature.	20
3.2	List of operating conditions for the study of the effect of catalyst concentration.	21
3.3	List of operating conditions for the study of the effect of methanol to oil molar ratio.	22
3.4	Operating conditions of gas chromatography column	23
3.5	Stock standards	24
3.6	Working standards	24
4.1	The comparison of the conversion of palm oil to methyl ester at different temperature.	26
4.2	The comparison of the conversion of palm oil to methyl ester with different methanol to oil molar ratio.	30
4.3	The comparison of the conversion of palm oil to methyl ester with different catalyst concentration.	33

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Transesterification reaction of vegetable oil with alcohol to ester and glycerol	11
3.1	The schematic diagram of batch transesterification system	20
4.1	The comparison of the conversion of palm oil to methyl ester at different temperature	27
4.2	The comparison of the conversion of palm oil to methyl ester with different methanol to oil molar ratio	31
4.3	The comparison of the conversion of palm oil to methyl ester with different catalyst concentration.	34

LIST OF SYMBOL

^{o}C	= Degree Celsius
%	= Percentage
$SnCl_2$	= Tin(II) Chloride
mL	= Mili-Liter
g	= Gram
kg	= kilograms
min	= Minutes
hr	= Hours
m	= Meter
µm	= Micron- meter
mm	= Mili-Meter
rpm	= Revolutions per minute
M	= Molar (mol/dm^3)
V	= Volume
FFA	= Free Fatty Acid

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Calibration curves of the methyl esters	43
B	Typical Analysis Calculation	47

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The world of energy demand is fulfilled by conventional energy sources like coal, petroleum, and natural gas. Petroleum based fuels are limited reserves concentrated in certain regions of the world. Besides that, the politic unstable situation in Middle East largely affects the price of the fuel. These sources are on the verge of researching their peak production. The scarcity of known petroleum reserves will make renewable energy sources more attractive (Sheehan *et a*l., 1998). Experts suggest that current oil and gas reserves would suffice to last only a few more decades (Demirbas 2007). To meet the rising energy demand, fuels such as biodiesel and bioethanol are in the forefront of alternative technologies. Accordingly, the viable alternative for compression ignition engines is biodiesel (Knothe *et al.*, 2001).

Biodiesel is defined as the monoalkyl esters of long chain fatty acids derived from the renewable biolipids via transesterification process of triglycerides or the esterification of free fatty acids with low molecular weight alcohols such as methanol and ethanol in the presence of a catalyst to yield methyl or ethyl esters and glycerine (Demirbas 2002). The use of vegetable oils and their derivatives as diesel fuel is a concept nearly as old as the diesel engine itself (Knothe *et al.*, 2001). At the Paris World Exhibition in 1990, the diesel engine was demonstrated using a vegetable oil (peanut oil) as fuel. Biodiesel production has increased significantly over the past few years. Current commercial production capacity on global scale is in the range of 800,000 tonnes (Anon 2001). Numerous biodiesel plants are under construction or in planning stages with accompanying significant increases in production capacity, particularly in Germany, United States, and Malaysia.

Various raw materials such as soybean oil (in United States), rapeseed oil (in Europe), palm oil (in Malaysia) and waste fat (in Japan) have all been employed (Gunstone 2004). The methyl esters can be used in partial or complete replacement of conventional diesel fuel without modification of the engine and without noticeable diminution of efficiency. Biodiesel is a non toxic product. It is 98 percent biodegradable in 21 days compared with 50 percent for normal diesel. It also performs satisfactorily in standard environmental tests with fish, bacteria and plants. Biodiesel produces less sulfur smoke, pollutants, unburnt fuel and polycyclic aromatic hydrocarbons when used in an engine and compared with mineral fuel.

Malaysia and Indonesia are starting pilot-scale biodiesel production from palm oil (Vijayalakshmi *et al.*, 2007). Malaysia has a rich oil palm industry that generates excess crude palm oil, in vast quantities for consumption every year. Besides that, crude palm oil is cheaper than other vegetables oil such as canola, rapeseed or soybean oil. It would reduce the overhead cost of biodiesel production and assure sufficient supply of the raw material.

1.2 Problem Statement

With the launching of the Envo Diesel (palm olein blend with diesel) in 2006, biodiesel has recently become very attractive in Malaysia. Currently, most biodiesel is prepared using alkaline catalysts or mineral acid catalysts. Nonetheless, the overall base-catalyzed process suffers from serious limitations that translate into high production costs for biodiesel. Strict feedstock specifications are a main issue with this process. In particular, the total FFA content associated with the lipid feedstock must not exceed 0.5 wt %. Otherwise, soap formation seriously hinders the production of fuel grade biodiesel. Besides that, the major drawbacks of using mineral acid catalysts are reactor corrosion problems and substantial generation of byproduct and wastes, including the salts formed as a result of the mineral acid neutralization, which must be disposed off into the environment, comprise negative and virtually impassable aspects for the mineral acid-catalyzed process.

The biodiesel manufacturing technique has to accomplish the reduction of waste pollutants provoked by conventional catalytic processes. Thus, the extensive demand for cleaner methodologies has forced the chemical industry to use environmentally friendly acidic catalysts. A highlighted example is the Lewis acid catalysts. These lewis acid catalysts, which normally present Lewis acidity, are easier to separate from the reaction medium and are potentially less corrosive for the reactors. Besides that, lewis acid catalysts are able to operate under mild conditions of reaction to achieve higher conversion of biodiesel production. Thus, using lewis acid catalysts in transesterification process allow the production of biodiesel in more competitive costs, in the processes which gives lower environmental impact.

1.3 Objective

The objective of this study is to

(a) To produce biodiesel from palm oil using Tin Chloride (II) as catalyst
(b) To achieve highest conversion of biodiesel with the optimum temperature, methanol to oil molar ratio and the catalyst concentration.

1.4 Scope of Research Work

In the present study, three parameters were investigated. These parameters are temperature, methanol to oil molar ratio and the catalyst concentration. The range of study for the temperature is 65 – 125 °C. For the methanol to oil molar ratio and the catalyst concentration, the value will be varied from 1:12 – 1:24 and 4 - 10% (by weight based on oil) respectively.

1.5 Rationale & Significance of Study

Worldwide production of vegetable oil and animal fat is not sufficient to replace liquid fossil fuel use. Thus, we need to utilize the vegetable oils as raw material to produce high amount of biodiesel and maximize the utilities of lewis acid catalyst in producing biodiesel. Besides that, we need to create a new catalyst development technology to solve the problems faced by conventional catalyst.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is briefly defined as the monoalkyl esters of vegetables oils or animal fats. Biodiesel is a clear amber-yellow liquid with a viscosity similar to that of petrodiesel. Biodiesel is non-flammable and, in contrast to petrodiesel, is non-explosive(Demirbas 2007). It is practically immiscible with water, has a high boiling point and low vapor pressure. Selected properties of diesel are compared to biodiesel fuels in Table 2.1.

Biodiesel which is 100% biodiesel fuel is referred to as B100 or 'neat' fuel. A biodiesel blend is pure biodiesel blended with biodiesel. Biodiesel required to meet the requirements of American Society of Testing and Materials (ASTM) specification designated in ASTM D- 6751. Blends of biodiesel with conventional diesel fuel have produced substantial improvements in combustion products similar to pure biodiesel. B100 is approximately four times more biodegradable than diesel and B20 twice as biodegradable. Normally, it is 98 per cent biodegradable in 21 days (Gunstone 2004). It can be used as an additive in formulations of diesel to increase the lubricity of pure Ultra Sulfur Diesel (ULSD) fuel. Some measurement and care need to take to ensure the biodiesel used does not affect the sulfur content of the mixture above 15 ppm.

Table 2.1: Specification of diesel and biodiesel fuel (Tyson, 2001)

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower hearing value (MJ/m^3)	36.6 x 10^3	32.6 x 10^3
Kinematic viscosity @ 40°C (mm^2/s)	1.3-4.1	1.9-6.0
Specific gravity @ 15.5 °C	0.85	0.88
Density @ 15 °C (kg/m^3)	848	878
Water (ppm by wt)	161	0.05% max
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (by diff.)(wt%)	0	11
Sulfur (wt%)	0.05 max	0.0-0.0024
Boiling point (°C)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiomeric air/fuel ratio (wt/wt)	15	13.8

Biodiesel is a clean-burning alternative fuel which is derivative of natural products since it has almost no sulphur, no aromatics (Tollefson 1993). Biodiesel burns like petroleum diesel as it involves regulated pollutants (Demirbas 2007). On the other hand, biodiesel has greater efficiency than gasoline. Biodiesel also exhibits great potential for compression-ignition engines. Biodiesel is now mainly being produced from soybean, rapeseed, and palm oils. The higher heating values (HHVs) of biodiesels are relatively high. The HHVs of biodiesels (39 to 41 MJ/kg) are slightly lower than those of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32 to 37 MJ/kg) (Demirbas 2007). Besides that, biodiesel will reduce approximately 50% carbon monoxide and 78% carbon dioxide emission on a net lifecycle basis. It happens because the carbon in biodiesel emissions is recycled from carbon that was in the atmosphere, rather than the carbon introduced from the petroleum that was sequestered in the earth's crust (Sheehan 1998).

2.2 Method of Producing Biodiesel

The vegetable oils and animal fats that contain free fatty acid, phospholipids, sterols, water, odourants and other impurities cannot be used as fuel directly. Generally there are five methods to produce biodiesel which are direct use and blending, pyrolysis (thermal) cracking, esterification and transesterification.

2.2.1 Direct Use and Blending

The direct usage of vegetable oils as biodiesel is possible by blending it with conventional diesel fuels in a suitable ratio and these ester blends are stable for short term usages (Srivathsan *et al.*, 2007). The blending process is simple which involves mixing alone and hence the equipment cost is low. The Prime Minister of Malaysia, Datuk Seri Abdullah Ahmad Badawi launched the the B5 palm oil-based biofuel called "Envo Diesel" in 21 March 2006 and implemented in stages starting with selected government vehicles and moving on to public use. Direct use of vegetable oils or the use of blends of the oils are not satisfactory and impractical for both direct and indirect diesel engines due to high viscosity, acid contamination, free fatty acid formation resulting in gum formation by oxidation and polymerization and carbon deposition (Ma *et al.*, 1998). Hence vegetables oils are processed so as to acquire properties (viscosity and volatility) similar to that of fossil fuels and the processed fuel can be directly used in the diesel engines available.

2.2.2 Micro-emulsion

Micro-emulsions are isotropic, clear, or translucent thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called cosurfactant (Schwab *et al.*, 1987). A micro-emulsion can be made of vegetable oils with an ester and dispersant (cosolvent), or of vegetable oils, an short-chain alcohol and a surfactant, with or without diesel fuels. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Pryde 1984). Microemulsions because of their alcohol content have lower volumetric heating values than diesel fuels, but the alcohols have high latent heat of vaporization and tend to cool the combustion chamber, which would reduce nozzle coking (Srivastava *et al.*, 1999). For example, the short term performances of both ionic and non-ionic microemulsions of aqueous ethanol in soybean oil were nearly as good as that of No. 2 diesel, in spite of the lower cetane number and energy content (Goering *et al.*, 1982).

2.2.3 Pyrolysis (Thermal Cracking)

Pyrolysis defined as the cleavage to smaller molecules by thermal energy (Madras *et al.*, 2004). Because of the possibility of producing triglycerides in a wide variety of products by high temperature pyrolysis reaction, many investigators have studied the pyrolysis of triglycerides to obtain products (liquid, gas, solid) suitable for fuel under different reaction conditions with and without catalyst (Lima *et al.*, 2003). Pyrolysis and catalytic cracking of oils and fats in the absence of oxygen result in production of alkanes, alkenes, alkadienes, cycloalkanes, alkylbenzenes, carboxylic acids, aromatics and small amounts of gaseous products. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses:

conventional pyrolysis, fast pyrolysis, and flash pyrolysis (Demirbas *et al.*, 2007). The three vegetable oils (soy bean, palm, and castor oils) were pyrolyzed to obtain light fuel product at 503 to 673 K (Lima *et al.*, 2003). These results show that palm oil reacts in a lower temperature range with a higher yield in the heavy fraction. A short pyrolysis time (less than 10 s) leads to a high amount of alkanes, alkenes, and aldehyde instead of carboxylic acids. On the other hand, higher temperature and long pyrolysis times do not favor an pyrolysis of this material. The liquid products can be improved by deoxygenation in order to obtain an enriched hydrocarbon diesel like fuel (Fortes 1999).

The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel (Ma *et al.*, 1999). Besides that, the pyrolysed vegetable oils possess acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values but unacceptable ash, carbon residue amounts and pour point (Srivastava *et al.*, 1999).

2.2.4 Esterification

The esterification is a reversible reaction where free fatty acids are converted to alkyl esters via catalysis. Either base or acid catalysts can be used for reaction. However, base catalysts can only be used at high temperature while acid catalysts are able to carry out under mild conditions (Spivey *et al.*, 2007). When oil are high in free fatty acids, the simultaneous esterification and transesterification reactions via acid catalysis is advantageous to potentially obtain nearly complete conversion to biodiesel (Drapcho *et al.*, 2007). The esterification process follows a similar reaction mechanism of acid catalyzed transesterification. The reactants including free fatty acids and alcohol are catalyzed by acid to create alkyl ester and water as shown in equation 2.1. Wang (2001) used 2 percent ferric sulfate as a catalyst to conduct esterification as a pretreatment step before transesterification and obtained 97 percent conversion of waste cooking oil high in free fatty acid.

$$RCOOH + R'OH \rightarrow RCOOR' + H_2O \qquad \text{(Equation 2.1)}$$

2.2.5 Transesterification

Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except than an alcohol is used instead of water (Srivastava *et al.*, 1999). This process has been widely used to reduce the viscosity of triglycerides so that the biodiesel produced by this process able to miscible with mineral diesel (Pinto *et al.*, 2005). The high viscosity of vegetable oils was the cause of severe operation problems such as engine deposits. Triacylglycerols (vegetable oils and fats) are esters of long-chain carboxylic acids combined with glycerol. Carboxylic acids can be converted into methyl esters by the action of a transesterification agent. It consists of a sequence of three consecutive reversible reactions where triglycerides are converted to diglycerides and then diglycerides are converted to monoglycerides followed by the conversion of monoglycerides to glycerol. In each step an ester is produced and thus three ester molecules are produced from one molecule of triglycerides (Sharma *et al.*, 2008). The formation of alkyl esters from monoglycerides is believed to be the step that determines the reaction rate since monoglycerides are the most stable intermediate compound (Ma *et al.*, 1998). Transesterification reaction of triglycerides with alcohol.is represented by the figure 2.1.

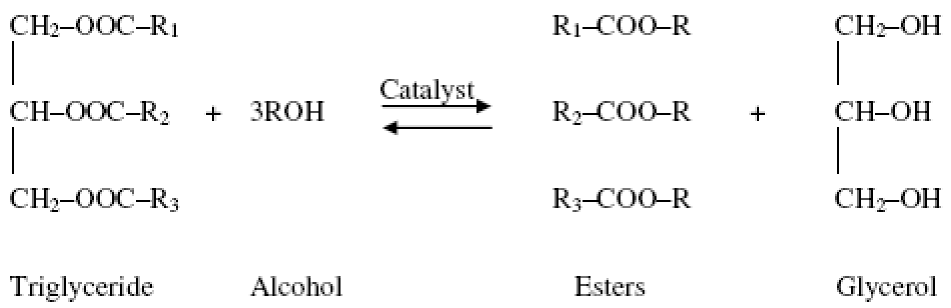

Figure 2.1: Transesterification reaction of vegetable oil with alcohol to ester and glycerol

Among all these alternatives, transesterification seems to be the best choice as the physical characteristics of fatty acid methyl esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. In the esterification of an acid, an alcohol acts as a nucleophilic reagent but in the hydrolysis of an ester, an alcohol is displaced by a nucleophilic reagent. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. Ma (1999) reported that the main factors affecting transesterification are molar ratio of glycerides to alcohol, catalysts, reaction temperature and time and the contents of free fatty acids and water in oils and fats. Higher reaction temperatures speed up the reaction and shorten the reaction time. The reaction is slow at the beginning for a short time and proceeds quickly and then slows down again. The commonly accepted molar ratio of alcohol to glycerides is 6:1. An excess of the alcohol favors the formation of alkyl esters (Ma *et al.*, 1998). Wang (2001) used five different temperatures from 77 to 117 °C in the transesterification of soybean oil to biodiesel. Increasing temperature had a marked effect on reaction rate with near complete conversion of soybean oil (96%) requiring only 3 hours at 117 °C, while comparable conversions at 77 °C required 20 hours.

Non-catalytic transesterification reaction is slow and normally needs high pressures and temperatures to be completed (Zabeti *et al.*, 2008). Yield is very low at temperatures below 350 °C and therefore higher temperatures were required.

However at temperature greater than 400 °C thermal degradation of esters occurred (Demirbas 2006). Kusdiana (1999) subjected rapeseed oil into transesterification process in the absence of catalyst and in the supercritical methanol and found that the amount of water in the reaction does not affect the conversion of oil. Kusdiana (1999) reported that the conversion of rapeseed oil can achieve the conversion of 73% at the temperatures of 350°C without catalyst.

2.3 Catalyst

Transesterification reaction can be either carried out via non-catalytic or catalytic processes. Base catalysts, acid catalysts and enzymes are three categories of catalysts which have been studied for biodiesel production. But the former two types are more popular in biodiesel industry due to their short reaction time and the low cost compared with the latter.

2.3.1 Homogeneous Catalyst

The usage of homogeneous catalyst gives some advantages such as cheaper and faster reaction rate, reaction condition at low temperature and pressure, yield high conversion with minimal side reaction, soluble in alcohol provide direct conversion to biodiesel yield and no exotic material of construction are needed. One of the major disadvantages of homogeneous catalysts is that they cannot be reused or regenerated, because the catalyst is used in the reaction and separation of catalyst from products is difficult and requires more equipment which could result in higher production costs (Freedman *et al.,* 1986). Besides, the process is not environmentally friendly because a large amount of waste water is produced in the separation step (Vicente *et al.*, 2004). Canakci and Van Gerpen (1998) studied how the reagent molar ratio affected reaction rates and product conversion in the homogeneous catalyzed transesterification of soybean oil. Five different molar ratios, from 3.3:1 to 30:1, were studied. Their results indicated that ester formation increased with increasing the molar ratio, reaching its highest value, 98.4%, at the highest molar ratio used, 30:1. They concluded that the homogeneous catalyszed transesterification required more alcohol as reagent than heterogeneous catalyzed transesterification.

2.3.1.1 Base-catalyzed Transesterification

Esters, in the presence of bases such as an alcoholate anion, form an anionic intermediate, which can dissociate back to original ester or form a new ester (Demirbas 2008). Currently, most commercially available biodiesel is produced by base-catalyzed processese that employ NaOH as the active catalyst due to its lower cost. The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. The first step is the reaction of the base with the alcohol, producing an alkoxide and a protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed. Diglycerides and monoglycerides are converted by the same mechanism into a mixture of alkyl esters and glycerol. Demirbas (2008) reported that alkaline metal alkoxides are the most active catalysts since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water and free fatty acid, which makes them inappropriate for typical industrial processes (Schuchardt *et al.*, 1998). Schuchardt (1998) studied the effect of Sodium Methoxide to the conversion of biodiesel. His results indicated that ester formation reaching its highest value, 97.8% in short reaction time (40 min), with a low molar ratio used, 4.5:1 using Sodium Mehoxide as catalyst.

2.3.1.2 Acid-catalyzed Transesterification

The transesterification process usually is catalyzed by Bronsted acids, preferably by sulfonic and sulfuric acids (Demirbas 2008). These catalysts give very high yields in alkyl esters, but the reactions is about 3 orders of magnitude slower than the alkali-catalyzed reaction for comparable amounts of catalyst (Freedman *et al.*, 1986). Although the yield of acid-catalyzed transesterification is high, the acids, being corrosive, may cause damage to the equipment and the reaction rate was also observed to be low (Freedman *et al.*, 1986). To overcome the disadvantages of acid catalyzed process or pretreatment, the homogeneous lewis acid catalyst (carboxylic salts) was used (Peng *et al.*, 1999). One of the advantage of acid catalyst is their low susceptibility to the presence of free fatty acid in the starting feedstock. However, acid catalyzed transesterification is sensitive to water concentration (Spivey *et al.*, 2007). Van Gerpen (1998) showed that as little as 0.1 wt% water in the reaction mixture was able to substantially affect ester yields in the transesterification of vegetable oil with methanol, with the reaction almost completely inhibited at 5wt% water concentration. Kusdiana and Saka published their results on the effect of water on methyl ester formation by the transesterification of rapeseed oil with methanol using base and acid (1.5 wt% NaOH and 3 wt% H_2SO_4). Their studies found that water concentration was more critical in acid catalysis than in base catalysis. This is because the transesterification of small esters under acid-catalyzed conditions was retarded by the presence of spectator polar compound.

Recently, some studies present the use of common Lewis acids eg. $AlCl_3$, $ZnCl_2$ in biodiesel synthesis primarily to demonstrate an alternative catalyst for the simultaneous esterification of long chain fatty acid and transesterification of vegetable oil. Sn, Pb and Zn complexes have been demonstrated to be effective in homogeneous lewis acid catalyzed transesterification of vegetable oil via the formation of a four-membered ring transition state (Soriano *et al.*, 2007). Soriano (2007) reported that the optimum conditions to afford 98% conversion of canola oil to methyl ester is with the use of 24 methanol to oil molar ratio and reaction time of